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# Atmospheric Chemistry of Gas-phase Polycyclic Aromatic Hydrocarbons: Formation of Atmospheric Mutagens

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The atmospheric chemistry of the 2- to 4-ring polycyclic aromatic hydrocarbons (PAH), which exist mainly in the gas phase in the atmosphere, is discussed. The dominant loss process for the gas-phase PAH is by reaction with the hydroxyl radical, resulting in calculated lifetimes in the atmosphere of generally less than one day. The hydroxyl (OH) radical-initiated reactions and nitrate ($NO_3$) radical-initiated reactions often lead to the formation of mutagenic nitro-PAH and other nitropolycyclic aromatic compounds, including nitrodibenzopyranones. These atmospheric reactions have a significant effect on ambient mutagenic activity, indicating that health risk assessments of combustion emissions should include atmospheric transformation products. — Environ Health Perspect 102(Suppl 4):117–126 (1994).

Key words: polycyclic aromatic hydrocarbons, nitro-polycyclic aromatic hydrocarbons, gas-phase reactions, mutagens, hydroxyl radical, nitrate radical

## Introduction

Polycyclic aromatic hydrocarbons (PAH) and certain nitro-polycyclic aromatic hydrocarbons (nitro-PAH) are emitted into the atmosphere from combustion sources (*1,2*). For many years, research concerning the health implications of PAH emissions has been conducted (*3*), and more recently the nitro-PAH have been studied (*2,4–6*). Ten years ago a warning was given that the health effects of not only the directly emitted carcinogenic and mutagenic PAH and nitro-PAH, but also of their atmospheric transformation products, need to be assessed (*7,8*).

The last decade has brought a gradual realization that the gas-phase atmospheric chemistry of the PAH has a significant impact on the mutagenic activity of ambient atmospheres, both for vapor phase and particle-associated mutagens. The majority of ambient nitro-PAH now are thought to be formed in the atmosphere from the gas-phase reactions of the PAH with four rings or less (*9–14*). Atmospheric reactions generally produce products of increased polarity (*15–18*). Recently this has been shown to account for the trend of increased polarity seen in the direct-acting mutagenicity of ambient particles in comparison with, for example, diesel particles (*19,20*). Based largely on work conducted at the Statewide Air Pollution Research Center, University of California, Riverside, over the past 10 years, our current knowledge of the atmospheric reactions and lifetimes of the gas-phase PAH, their formation of mutagenic products, and the contributions of these products to the mutagenic activity of ambient atmospheres will be discussed.

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## Phase Distribution of PAH and PAH-derivatives in the Atmosphere

The PAH, nitro-PAH, and other polycyclic aromatic compounds (PAC) present in the atmosphere are distributed between the gas and particle phases, with this gas- or particle-phase distribution depending mainly on the liquid-phase vapor pressure of the PAH or PAC at the temperature of the ambient air parcel containing them (*21*). As discussed by Bidleman (*21*) and Pankow and Bidleman (*22*), organic compounds with liquid-phase vapor pressures greater than $10^{-6}$ Torr at the ambient air temperature will exist, at least partially, in the gas phase in the atmosphere. The subcooled liquid vapor pressures of the 2- to 4-ring PAH are greater than or equal to $10^{-6}$ torr at 298 K, and ambient air measurements (*23–28*) have shown that the 2- to 4-ring PAH, as well as the 2-ring nitro-PAH, are largely gas-phase species.

Table 1 shows the measured ambient air concentrations of a series of PAH and nitro-PAH collected on Teflon-coated glass fiber filters compared with the total ambient air concentrations from collections on filters, polyurethane foam, and Tenax solid adsorbents (*24*). These and other data (*24,26,28*) show that the 4-ring PAH fluoranthene and pyrene are mainly (greater than or equal to 90% as calculated from the measured filter and solid adsorbent concentrations) in the gas phase at the ambient air temperatures typically encountered in California. Even at ambient air temperatures of approximately 0°C, 30 to 70% of the fluoranthene and pyrene were collected on the polyurethane foam adsorbent located downstream from the filters (*26*).

## Laboratory Studies of Atmospheric Reactions of PAH and Formation of Nitro-PAH

As for other classes of organic compounds, the gas-phase PAH and nitro-PAH can undergo wet and dry deposition (*16,21*), photolysis, and gas-phase reactions with OH radicals, $NO_3$ radicals, and $O_3$ (*16,29–32*). For the gas-phase PAH, dry deposition is

**Table 1.** Particle-associated (filter) and total atmospheric (sum of filter and solid adsorbent) concentrations of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons in a daytime sample collected at El Camino Community College, Torrance, CA, February 25, 1986, 6:00 A.M. to 6:00 P.M. (*24*).

| Compound | Molecular weight | ng $m^{-3}$ Filter | ng $m^{-3}$ Σ (Filter + solid adsorbent) |
|---|---|---|---|
| PAH | | | |
| Naphthalene | 128 | 0.45 | 3300 |
| Phenanthrene | 178 | 0.33 | 78 |
| Anthracene | 178 | 0.03 | 6.1 |
| Fluoranthene | 202 | 0.47 | 8.0 |
| Pyrene | 202 | 0.60 | 8.0 |
| Benzo[*a*]pyrene | 252 | 0.59 | 0.6 |
| Perylene | 252 | 0.18 | 0.2 |
| Nitro-PAH | | | |
| 1-Nitronaphthalene | 173 | 0.05 | 3.0 |
| 2-Nitronaphthalene | 173 | 0.006 | 2.9 |
| 3-Nitrobiphenyl | 199 | 0.03 | 6.0 |
| 9-Nitroanthracene | 223 | 0.05 | 0.05 |
| 2-Nitrofluoranthene | 247 | 0.28 | 0.3 |
| 1-Nitropyrene | 247 | 0.04 | 0.04 |
| 2-Nitropyrene | 247 | 0.04 | 0.04 |

PAH, polycyclic aromatic hydrocarbon.

**Table 2.** Room temperature rate constants, *k*, for the gas-phase reactions of OH radicals, $NO_3$ radicals, and $O_3$ with PAH and nitro-PAH.

| | *k*($cm^3$ molecule$^{-1}$ s ec$^{-1}$) for reaction with OH[a] | $NO_3$[b] | $O_3$[c] |
|---|---|---|---|
| PAH | | | |
| Naphthalene | $2.16 \times 10^{-11}$ | $3.6 \times 10^{-28}[NO_2]$ | $<2 \times 10^{-19}$[d] |
| 1-Methylnaphthalene | $5.3 \times 10^{-11}$ | $7.7 \times 10^{-28}[NO_2]$ | $<1.3 \times 10^{-19}$ |
| 2-Methylnaphthalene | $5.2 \times 10^{-11}$ | $1.08 \times 10^{-27}[NO_2]$ | $<4 \times 10^{-19}$ |
| Biphenyl | $7.2 \times 10^{-12}$ | $<5 \times 10^{-30}[NO_2]$ | $<2 \times 10^{-19}$[d] |
| 2,3-Dimethylnaphthalene | $7.7 \times 10^{-11}$ | $1.55 \times 10^{-27}[NO_2]$ | $<4 \times 10^{-19}$ |
| Acenaphthene | $1.0 \times 10^{-10}$ | $\{4.6 \times 10^{-13} + 1.7 \times 10^{-27}[NO_2]\}$ | $<5 \times 10^{-19}$ |
| Acenaphthylene | $1.1 \times 10^{-10}$ | $5.5 \times 10^{-12}$ | $5.5 \times 10^{-16}$ |
| Fluorene | $1.3 \times 10^{-11}$ | | |
| Phenanthrene | $3.1 \times 10^{-11}$ | | |
| Anthracene | $1.3 \times 10^{-10}$[e] | | |
| Fluoranthene | | $5.1 \times 10^{-28}[NO_2]$ | |
| Pyrene | | $1.6 \times 10^{-27}[NO_2]$ | |
| Nitro-PAH | | | |
| 1-Nitronaphthalene | $5.4 \times 10^{-12}$ | $3.0 \times 10^{-29}[NO_2]$ | $<6 \times 10^{-19}$ |
| 2-Nitronaphthalene | $5.6 \times 10^{-12}$ | $2.7 \times 10^{-29}[NO_2]$ | $<6 \times 10^{-19}$ |
| 2-Methyl-1-nitronaphthalene | $<8.3 \times 10^{-12}$ | $\{1.1 \times 10^{-14} + 2.7 \times 10^{-29}[NO_2]\}$ | $<3 \times 10^{-19}$ |

PAH, polycyclic aromatic hydrocarbon. [a] Taken from Atkinson (*29*). [b] Taken from Atkinson (*31*); $NO_2$ concentrations in molecule $cm^{-3}$ units. [c] Taken from Atkinson (*32*) except as indicated. [d] Taken from Atkinson et al. (*44*). [e] At 298 K, estimated from data obtained at 325 K.

expected to be of little importance (*33*), and based on the wash-out ratios measured by Ligocki et al. (*34*), wet deposition is expected to be of minor importance as an atmospheric loss process for gas-phase PAH. After the origin of each reactive species is noted, the individual gas-phase reaction processes are discussed below.

Ozone concentrations in the unpolluted troposphere are typically about $7 \times 10^{11}$ molecule $cm^{-3}$ (30 ppb mixing ratio at ground level) (*35*). The photolysis of $O_3$ in the troposphere to yield the $O(^1D)$ atom leads to the formation of the OH radical:

$$O_3 + h\nu\ (\lambda < 320\ \text{nm}) \rightarrow O_2(^1\Delta_g) + O(^1D)$$
$$O(^1D) + H_2O \rightarrow 2\ OH$$
$$O(^1D) + M \rightarrow O(^3P) + M$$
$$(M = N_2, O_2, \text{and } CO_2)$$

From consideration of the estimated emissions of $CH_3CCl_3$ into the atmosphere, the atmospheric concentrations of $CH_3CCl_3$, and a knowledge of the rate constant for reaction of $CH_3CCl_3$ with the OH radical (the major tropospheric loss process for $CH_3CCl_3$), Prinn et al. have obtained an annually, seasonally and diurnally, averaged global tropospheric OH radical concentration of $8 \times 10^5$ molecule $cm^{-3}$ (*36*).

The $NO_3$ radical is formed from the sequence of reactions

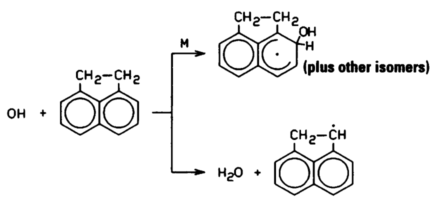
$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + NO \rightarrow 2\ NO_2$$
$$NO_3 + h\nu \rightarrow NO_2 + O(^3P)$$
$$NO_3 + h\nu \rightarrow NO + O_2$$
$$NO_3 + NO_2 \leftrightarrow N_2O_5$$

Because of the rapid photolysis of the $NO_3$ radical (with a photolysis lifetime at solar noon of approximately five sec) and the rapid reactions of NO with $O_3$ and of the $NO_3$ radical with NO (*37*), $NO_3$ radical concentrations are low during daylight hours. In the presence of $NO_2$ and $O_3$, $NO_3$ radical concentrations generally increase over continental areas after sunset (*38,39*). Based on the available data, Atkinson (*31*) suggested an average $NO_3$ radical concentration in the lower troposphere during nighttime hours of approximately $5 \times 10^8$ molecule $cm^{-3}$ (approximately 20 ppt) over continental areas. Over marine areas, $NO_3$ radical concentrations are lower [approximately 0.25 ppt at 3 km altitude near Hawaii (*40*)], as expected because of the low $NO_2$ concentrations (*40,41*).

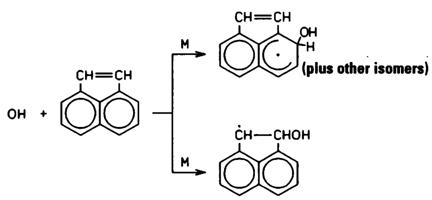
The reactions of the 2- to 4-ring PAH and 2-ring nitro-PAH that may be important in the atmosphere have been studied experimentally under laboratory conditions (*9,11–14,19,20,42–59*). The kinetic and product data from these studies, combined with our understanding of the atmospheric chemistry of other classes of organic compounds (*30,32*), allow a reasonably consistent, though still incomplete, understanding of the atmospheric chemistry of the 2- to 4-ring PAH and 2-ring nitro-PAH. The individual reaction processes are discussed below.

## Reactions of Gas-phase PAH and Nitro-PAH with the OH Radical

The rate constants for the gas-phase reactions of the OH radical with PAH and nitro-PAH are given in Table 2. Only for naphthalene, biphenyl, and phenanthrene have studies been conducted by more than one research group, and the rate constants given in Table 2 for these three PAH are the recommended values of Atkinson (*29*). As discussed by Atkinson (*29*), the OH radical reactions with the PAH and PAH-derivatives proceed by two reaction pathways: OH radical addition to the aromatic ring to form an initially energy-rich hydroxycyclohexadienyl-type radical and OH radical interaction with the substituent groups, either through H-atom abstraction from C–H bonds or OH radical addition to >C = C<bonds. For example, for acenaphthene, the reactions are




and for acenaphthylene the reactions are




For the alkyl-substituted PAH such as 1- and 2-methylnaphthalene, 2,3-dimethylnaphthalene, and (probably) acenaphthene, the reaction pathway involving OH radical addition to the aromatic ring dominates under atmospheric conditions (*29*). For those PAH containing unsaturated cyclopenta-fused rings (acenaphthylene and acephenanthrylene), OH radical addition to the cyclopenta-fused ring >C = C<bond may be significant.

The products of these OH radical-initiated reactions are not well understood. The observed products of the OH radical-initiated reactions (in the presence of $NO_x$) of naphthalene and biphenyl are hydroxy- and nitro-PAH (*52*). The yields of the naphthols are 7 and 4% for 1- and 2-naphthol, respectively, significantly higher than the 1- and 2-nitronaphthalene yields of approximately 0.3% each (*52*). Similarly, the yield of 2-hydroxybiphenyl from biphenyl is 20% (also with much lower amounts of 3- and 4-hydroxybiphenyl being produced), while the single nitro-derivative observed is 3-nitrobiphenyl in approximately 5% yield (*52*).

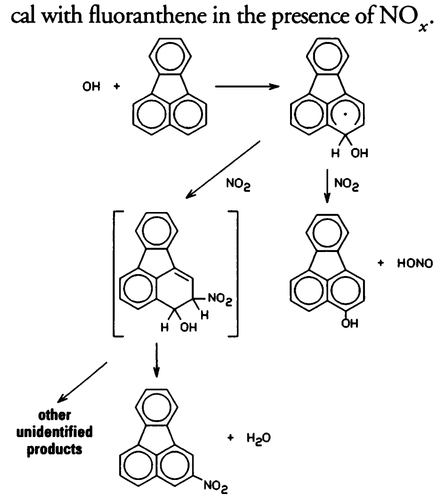
The specific nitro-PAH isomers formed from the gas-phase OH radical-initiated reactions of naphthalene (*52*), 1- and 2-methylnaphthalene (*11*), biphenyl (*12,52*), acenaphthene (*12*), acenaphthylene (*12*), fluorene (*58*), phenanthrene (*12*), anthracene (*12*), acephenanthrylene (*55*), fluoranthene (*9,14*), and pyrene (*9,14*), as well as their product yields, are given in Table 3. It should be noted that the nitrofluoranthenes and nitropyrenes formed from the gas-phase reactions of fluoranthene and pyrene have sufficiently low vapor pressures that they condense onto particles in the atmosphere, and at least for the 4-ring PAH, particle-phase nitro-PAH are formed from gas-phase PAH precursors.

**Table 3.** Nitroarene products formed from the gas-phase reactions of polycyclic aromatic hydrocarbons known to be present in ambient air with hydroxyl radicals and nitrate radicals (both in the presence of $NO_x$) and their yields.

| | Reaction with | |
|---|---|---|
| PAH | OH | $NO_3$ |
| Naphthalene | 1-Nitronaphthalene (0.3%)<br>2-Nitronaphthalene (0.3%) | 1-Nitronaphthalene (17%)<br>2-Nitronaphthalene (7%) |
| 1-Methylnaphthalene | All 1-methylnitronaphthalene isomers except 1-methyl-2-nitronaphthalene (≈ 0.4%) | All 1-methylnitronaphthalene isomers (≈30%) |
| 2-Methylnaphthalene | All 2-methylnitronaphthalene isomers except 2-methyl-1- and 2-methyl-3-nitronaphthalene (≈ 0.2%) | All 2-methylnitronaphthalene isomers (≈30%) |
| Acenaphthene | 5-Nitroacenaphthene<br>3-Nitroacenaphthene<br>4-Nitroacenaphthene } (Σ≈ 0.2%) | 4-Nitroacenaphthene (40%)[a]<br>3-Nitroacenaphthene (≈ 2%)[a]<br>5-Nitroacenaphthene (≈ 1.5%)[a] |
| Acenaphthylene | 4-Nitroacenaphthylene (2%) | No nitroisomers formed |
| Fluorene | 3-Nitrofluorene (≈ 1.4%)<br>1-Nitrofluorene (≈ 0.6%)<br>4-Nitrofluorene (≈ 0.3%)<br>2-Nitrofluorene (≈ 0.1%) | |
| Phenanthrene | Two nitroisomers (not 9-nitrophenanthrene) in trace yields | Four nitroisomers (including 9-nitrophenanthrene) in trace yields |
| Anthracene[b] | 1-Nitroanthracene, low yield<br>2-Nitroanthracene, low yield | 1-Nitroanthracene, low yield<br>2-Nitroanthracene, low yield |
| Pyrene | 2-Nitropyrene (≈ 0.5%)<br>4-Nitropyrene (≈ 0.06%) | 4-Nitropyrene (≈ 0.06%) |
| Fluoranthene | 2-Nitrofluoranthene (≈ 3%)<br>7-Nitrofluoranthene (≈ 1%)<br>8-Nitrofluoranthene (≈ 0.3%) | 2-Nitrofluoranthene (≈ 24%) |
| Acephenanthrylene | Two nitroarene isomers (≈ 0.1%) | None observed |
| Biphenyl | 3-Nitrobiphenyl (5%) | No reaction observed |

PAH, polycyclic aromatic hydrocarbon. [a] Yields for the $NO_3$ radical addition pathway to the fused aromatic rings (*12*). Reaction expected to proceed by H-atom abstraction from the C–H bonds of the cyclopenta-fused ring under atmospheric conditions. [b] 9-Nitroanthracene was observed in both the OH and $NO_3$ radical reactions, but may not be a product of these reactions because it is also formed from exposure to $NO_2$/$HNO_3$.

The available product data for the monocyclic aromatic hydrocarbons and biphenyl (*52,60,61*) indicate that the nitroarene product yields do not extrapolate to zero at low $NO_2$ concentrations and that the nitroarene formation yields determined under laboratory conditions (Table 3) may be applicable to ambient atmospheric conditions (*52,60,61*). The nitroarene product formation yields are low in all cases, ranging from less than or equal to 0.2 to 5%, and as noted above, the hydroxy-PAH yields for naphthalene and biphenyl are a factor of approximately 5 to 10 higher than the nitro-PAH yields. It is important to note that the majority of the OH radical-initiated reaction products of the PAH remain unidentified. While there are uncertainties about the reaction mechanisms, a recently postulated mechanism (*60*) that is consistent with our product data (*9,14*) is shown below for the reaction of the OH radical with fluoranthene in the presence of $NO_x$.



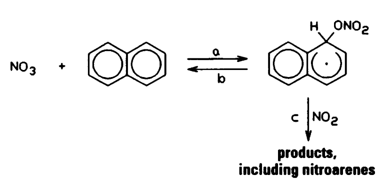

The nitroarenes formed from the OH radical-initiated reactions of the PAH (Table 3) are often isomers distinct from those observed in direct emissions such as diesel exhaust particles. For example, the most abundant nitro-isomers of pyrene, fluorene, and fluoranthene observed in diesel exhaust are 1-nitropyrene, 2-nitrofluorene, and 3-nitrofluoranthene, respectively (*62–65*), while the isomers formed from the gas-phase OH radical-initiated reactions of these PAH are 2-nitropyrene (*9,14*), 3-nitrofluorene (*58*), and 2-nitrofluoranthene (*9,14*), respectively. To date, there is no convincing evidence for significant artifact formation of nitro-PAH during atmospheric sampling, at least when using standard high-volume samplers (*66*).

## Reactions of Gas-phase PAH and Nitro-PAH with the $NO_3$ Radical

Naphthalene and the alkyl-substituted naphthalenes are observed to react in $N_2O_5$–$NO_3$–$NO_2$-air mixtures, in which $NO_3$ radicals are generated by the thermal decomposition of $N_2O_5$:

$$N_2O_5 \rightarrow NO_3 + NO_2.$$

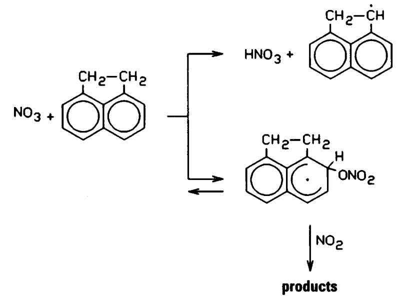
The disappearance rates of the naphthalenes relative to those of alkenes such as propene and *trans*-2-butene in these reaction mixtures as a function of the $NO_2$ concentration indicate that the PAH-loss processes are kinetically equivalent to reaction with $N_2O_5$ (*48,52–54,57*). The experimental data (*57*) show that the reaction of naphthalene in $N_2O_5$–$NO_3$–$NO_2$ air mixtures occurs by the initial addition of the $NO_3$ radical to the aromatic rings to form a nitratocyclohexadienyl-type radical, which then either decomposes back to reactants or reacts exclusively with $NO_2$.




The measured rate constant $k_{obs}$ for reaction with the $NO_3$ radical is

$$k_{obs} = \{(-d[\mathrm{PAH}]/dt)/[\mathrm{PAH}][NO_3]\} \\ = k_a k_c [NO_2]/k_b. \quad [1]$$

For those PAH containing substituent groups, a parallel reaction pathway involving $NO_3$ radical reaction with the substituent group(s) also can occur (*12,54*) in addition to $NO_3$ radical addition to the aromatic ring. For example, the reaction for acenaphthene is




and for acenaphthylene $NO_3$ radical addition to the cyclopenta-fused >C = C< bond is the dominant reaction pathway (*54*) [and presumably also for acephenanthrylene (*55*)]. Table 2 gives the available rate constants for the $NO_3$ radical reactions with the PAH and nitro-PAH.

The reactions which involve the initial addition of the $NO_3$ radical to the aromatic ring lead to the formation of nitroarenes (*11,12,14,48,49,52*), and these nitroarene yield data are given in Table 3. The reaction routes involving $NO_3$ radical interaction with the substituent group(s) do not lead to the formation of nitroarenes (*12*), as expected from the likely subsequent chemistry (*30*). The other products of these gas-phase $NO_3$ radical-initiated reactions of the PAH are presently not known with any certainty, although they may include hydroxynitro-PAH.

## Reactions of Gas-phase PAH and Nitro-PAH with $O_3$

The available rate constant data for reaction of PAH with $O_3$ are given in Table 2. A gas-phase reaction has been observed only for acenaphthylene (*54*), and reaction is expected to occur for acephenanthrylene also (*55*). Clearly, these PAH react with $O_3$ by addition of $O_3$ at the cyclopenta-fused ring >C = C< bond (*54*).

## Photolysis of Gas-phase PAH and Nitro-PAH

No evidence has been observed for the gas-phase photolysis of the 2- to 4-ring PAH (*44,46,50,54*). However, photolysis of 1- and 2-nitronaphthalene and 2-methyl-1-nitronaphthalene has been observed under ambient outdoor sunlight conditions (*13,56*). Photolysis of 1-nitronaphthalene, 2-methyl-1-nitronaphthalene and 2-, 7-, and 8-nitrofluoranthene also has been observed in an indoor chamber with black light irradiation (*13,14,56*), with the photolysis rates of the 1-nitronaphthalene and 2-methyl-1-nitronaphthalene in the indoor chamber being approximately one order of magnitude higher than under ambient conditions (*13,56*). The photolysis rates calculated for ambient tropospheric conditions [$J(NO_2) = 5.2 \times 10^{-3}\,\mathrm{sec}^{-1}$; 12-hr average] for 1-nitronaphthalene, 2-nitronaphthalene, and 2-methyl-1-nitronaphthalene are $(1.66 \pm 0.13) \times 10^{-4}\,\mathrm{sec}^{-1}$, $(1.28 \pm 0.10) \times 10^{-4}\,\mathrm{sec}^{-1}$, and $(1.3 \pm 0.4) \times 10^{-4}\,\mathrm{sec}^{-1}$, respectively (*13*). Nitro-PAH that are particle-associated under atmospheric conditions may be fully or partially protected from photolysis (*13,67–70*).

## Calculated Atmospheric Lifetimes of Gas-phase PAH and Nitro-PAH

The photolysis and reaction rate data given above can be combined with the ambient radiation flux and the ambient concentrations of OH and $NO_3$ radicals, $NO_2$ and $O_3$ to allow the estimation of the lifetimes of the PAH and nitro-PAH with respect to each of these tropospheric loss processes. These calculated lifetimes are given in Table 4. For the PAH not containing cyclopenta-fused rings, the dominant tropospheric loss process is by reaction with the OH radical, with calculated lifetimes of one day or less (note that OH radical reaction only occurs during daylight hours). The PAH containing cyclopenta-fused rings such as acenaphthene and acenaphthylene react with $NO_3$ radicals at a significant rate. The reaction pathway involving $NO_3$ radical addition to the fused rings of the PAH is not a significant tropospheric loss process for any of the gas-phase PAH. PAH having unsaturated cyclopenta-fused rings, such as acenaphthylene, acephenanthrylene, and cyclopenta[*c,d*]pyrene, react, or are expected to react, with $O_3$ at a significant rate.

In contrast to $O_3$ and the OH radical, which are ubiquitous at reasonably consistent (on a day-to-day level) ambient concentrations (*28,35,36*), the ambient concentrations of the $NO_3$ radical in the lower troposphere over continental areas exhibit large variations, with the mixing ratios ranging from less than 2 to 430 ppt (*71*). The ambient tropospheric concentration of the $NO_3$ radical at any given time (during nighttime) and place must be viewed as uncertain by a factor of at least 10. A good approximation is that the dominant tropospheric removal process for the PAH is by daytime reaction with the OH radical, leading to lifetimes of approximately 8 hr or less.

As seen from the rate-constant data given in Table 2 and the calculated lifetimes in Table 4, the presence of the nitro substituent group in the nitroarenes leads to a marked decrease in their reactivity toward the OH radical. To date, kinetic and product studies have been carried out only for three gas-phase, fused-ring nitroarenes (*13,56*), and photolysis will be the dominant tropospheric removal process for these compounds, with calculated lifetimes of approximately 2 hr.

## Evidence from Ambient Data for Transformations of Gas-phase PAH and Mutagen Formation

The recent ambient air measurement study of Arey et al. (*28*) provided clear evidence for the reactions of the volatile PAH with the OH radical, with the nighttime/daytime concentration ratios exhibiting a linear correlation with the OH radical reaction rate constant (Figure 1). From an estimate of the nighttime dilution rate provided by the daytime/nighttime ratio of 3-nitrobiphenyl [a nitro-PAH believed to be formed only in the atmosphere from the daytime reaction of biphenyl with the OH radical in the presence of $NO_x$ (*52*)], an average 12-hr daytime OH radical concentration of $2.2 \times 10^6$ molecule $cm^{-3}$ (during August) was derived, uncertain to at least a factor of 2 (*28*). This estimated OH radical concentration in an urban area is similar to the annually averaged global tropospheric 12-hr daytime OH radical concentration of $1.6 \times 10^6$ molecule $cm^{-3}$ (*36*) and provides very strong evidence that the gas-phase PAH do react in the troposphere.

Furthermore, the specific isomers of the nitro-PAH and nitro-PAC observed in ambient air suggest that they are formed in the atmosphere through the gas-phase reactions of the 2- to 4-ring PAH (*9,13,19,24–26,28,49,52,55,58,59,72–78*). Thus, ambient air contains nitro-PAH isomers distinct from the PAH electrophilic nitration products reported in direct emissions. The nitro-PAH isomers not formed from electrophilic nitrations are observed, however, in laboratory simulations of the atmospheric reactions of the PAH, providing strong evidence for atmospheric formation of nitro-PAH. For example, Figure 2 shows a combined gas chromatography-mass spectrometry single ion trace (GC-MS SIM) for the m/z 247 nitro-PAH (nitrofluoranthenes, nitropyrenes, and nitroacephenanthrylenes) present in an extract of a diesel exhaust particle sample and in an extract of an ambient air sample collected on filters. Figure 2 clearly shows that the ambient air particle sample contains several other nitrofluoranthenes and nitropyrenes in addition to the 1-nitropyrene expected to be a direct emission (as shown by the GC-MS SIM trace for the diesel exhaust particle sample in Figure 2). Furthermore, the additional nitrofluoranthenes (in particular the 2-nitrofluoranthene) and nitropyrenes are precisely those nitrofluoranthenes and nitropyrenes formed from the gas-phase OH radical-initiated reactions of fluoranthene and pyrene. [A further small peak on the GC-MS trace that elutes between 8-nitrofluoranthene and 4-nitropyrene is a nitroacephenanthrylene formed from the OH radical-initiated reaction of acephenanthrylene (*55*).]

We have observed that the 2-nitrofluoranthene concentration in ambient air samples consistently is higher than the directly emitted 1-nitropyrene concentration (*9,10,24,26*), showing the importance of atmospheric transformations of the 4-ring PAH with respect

**Table 4.** Calculated atmospheric lifetimes of polycyclic aromatic hydrocarbons (PAH) and PAH-derivatives due to photolysis and gas phase reaction with OH and $NO_3$ radicals and $O_3$.

| | Lifetime due to reaction with | | | |
|---|---|---|---|---|
| PAH | OH [a] | $NO_3$ [b] | $O_3$ [c] | Photolysis [d] |
| Naphthalene | 8.0-hr | 1.5 years | >80 days | |
| 1-Methylnaphthalene | 3.3-hr | 250 days | >125 days | |
| 2-Methylnaphthalene | 3.3-hr | 180 days | >40 days | |
| 2,3-Dimethylnaphthalene | 2.3-hr | 125 days | >40 days | |
| Biphenyl | 2.0 days | >105 years | >80 days | |
| Acenaphthene | 1.7-hr | 1.2-hr | >30 days | |
| Acenaphthylene | 1.6-hr | 6 min | ≈43 min | |
| Fluorene | 1.1 days | | | |
| Phenanthrene | 5.6-hr | | | |
| Anthracene | 1.3-hr | | | |
| Fluoranthene | ≈3.5-hr[e] | ≈85 days | | |
| Pyrene | ≈3.5-hr[e] | ≈30 days | | |
| 1-Nitronaphthalene | 2.7 days | 18 years | >28 days | 1.7-hr |
| 2-Nitronaphthalene | 2.6 days | 20 years | >28 days | 2.2-hr |
| 2-Methyl-1-nitronaphthalene | >1.7 days | 4.2 days | >55 days | 2.1-hr |

[a] For a 12-hr daytime average OH radical concentration of $1.6 \times 10^6$ molecule $cm^{-3}$ (*36*). [b] For a 12-hr average nighttime $NO_3$ radical concentration of $5 \times 10^8$ molecule $cm^{-3}$ (*31*) and an $NO_2$ concentration of $2.4 \times 10^{11}$ molecule $cm^{-3}$. [c] For a 24-hr average $O_3$ concentration of $7 \times 10^{11}$ molecule $cm^{-3}$ (*35*). [d] For an average 12-hr daytime $NO_2$ photolysis rate of $J(NO_2) = 5.2 \times 10^{-3}$ $sec^{-1}$. [e] Using estimated OH radical reaction rate constant of $5 \times 10^{-11}$ $cm^3$ $molecule^{-1}sec^{-1}$ based on rate constant correlation with ionization potential (*46*).

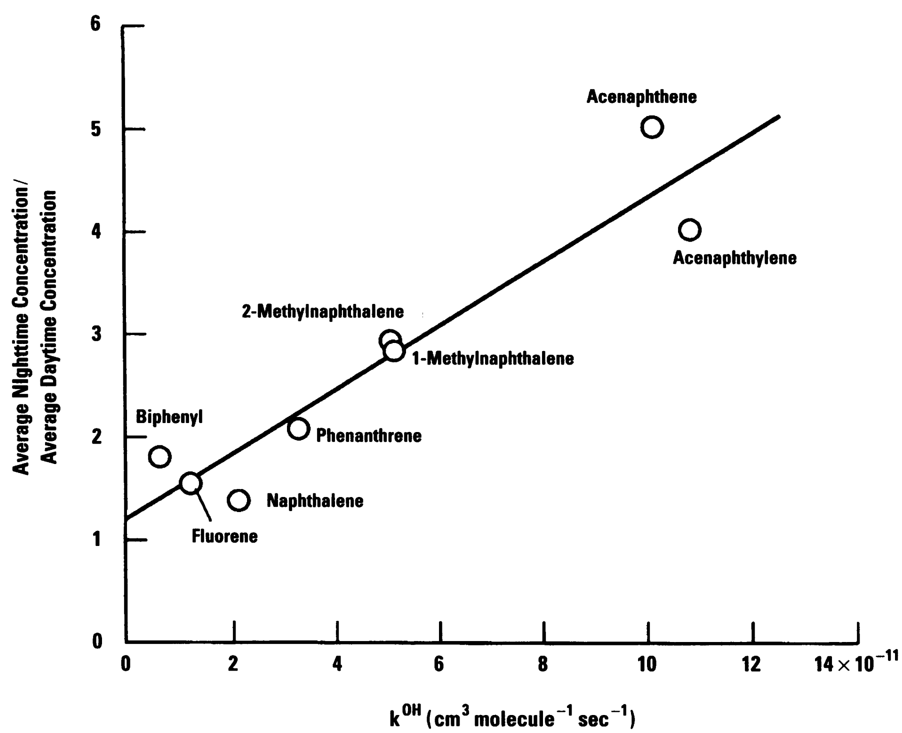



**Figure 1.** Plot of the average nighttime/average daytime concentrations of gas-phase PAH against their OH radical reaction rate constants. Data from Glendora, California, during August 1986 (*28*).

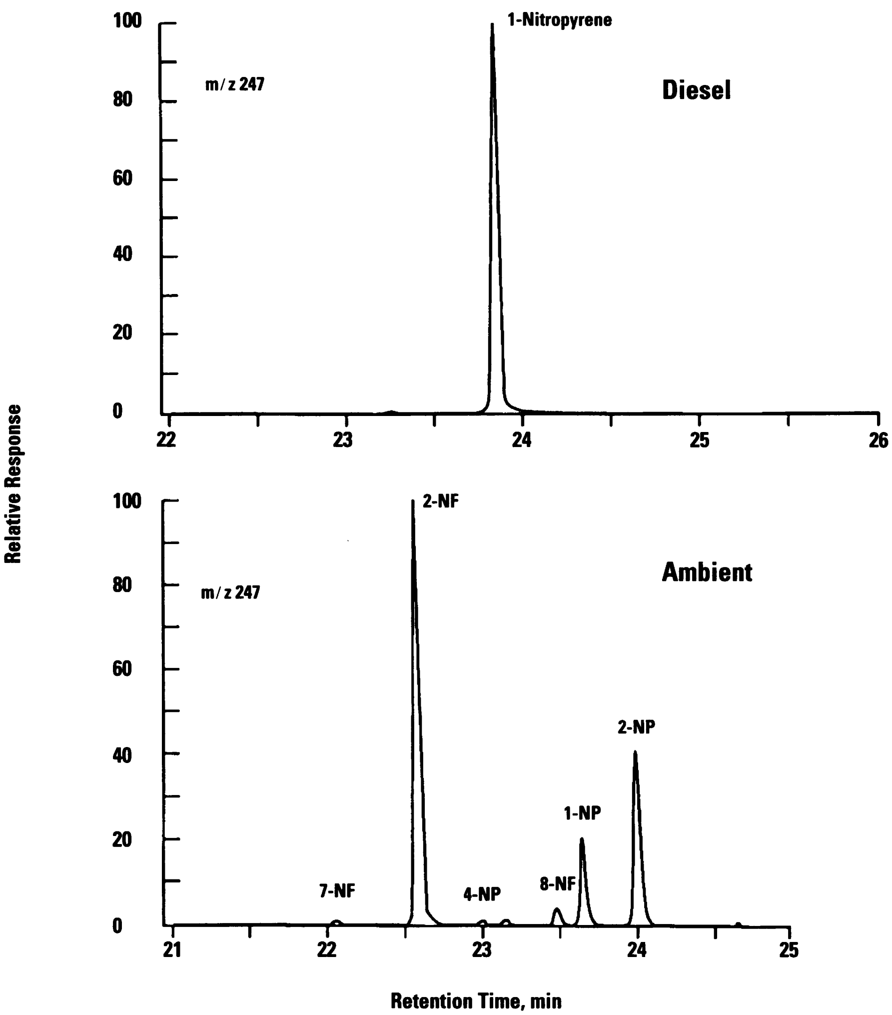



**Figure 2.** GC-MS SIM traces for the molecular ions of the nitrofluoranthenes (NF) and nitropyrenes (NP) in extracts from diesel particules and ambient particles (*24*) collected on filters in Torrance, California.

**Table 5.** Comparison of measured and calculated ambient nitroarene concentrations at Glendora, California, in August 1989 (*13*).

| | 12-hr average daytime concentration, ng $m^{-3}$ | |
|---|---|---|
| | Measured | Calculated |
| 1- + 2-Nitronaphthalene | 4.7 | 8.0 |
| 3-Nitrobiphenyl | 1.0 | 1.2 |
| 2-Nitrofluoranthene | 0.27 | 0.41 |
| 2-Nitropyrene | 0.012 | 0.040 |

to the formation of particle-associated nitro-PAH of molecular weight 247 (the major particle-associated nitro-PAH observed in ambient air).

The importance of atmospheric formation of nitroarenes is illustrated further in a comparison of the calculated and observed 3-nitrobiphenyl, 1- + 2-nitronaphthalene, 2-nitrofluoranthene, and 2-nitropyrene concentrations at Glendora, California (*13*). The predicted concentrations of these nitroarenes were calculated from the reaction rate constants and nitroarene product formation yields of the OH radical-initiated reactions of biphenyl, naphthalene, fluoranthene, and pyrene, respectively, using the estimated OH radical concentration at Glendora (*28*) and the measured ambient parent PAH concentrations (*28*), and incorporating the photolysis loss of the nitronaphthalenes. Using the rate constant and product yield data given in Tables 2 and 3 and the measured or estimated ambient PAH and OH radical concentrations (*28*), there is strikingly good agreement between the calculated and measured nitroarene concentrations at this site (Table 5). Only the nitronaphthalenes are expected to be present in direct emissions such as diesel exhaust, and the predicted concentrations for the nitronaphthalenes, which were slightly higher than the observed concentrations, suggest that atmospheric formation of these species dominates over their direct emission, at least for this site at the time of the measurements.

## Contribution of PAH Transformation Products to Ambient Direct-acting Mutagenicity

It has been known for many years that extracts of ambient air particles are carcinogenic (*79*) and mutagenic (*80–87*). Using the microsuspension modification of the Ames *Salmonella typhimurium* assay (*88*), we have measured (*89*) the direct-acting (in the absence of microsomal activation) mutagenicity of extracts of ambient air samples collected on Teflon-coated glass fiber filters (particle phase) and polyurethane foam (PUF) plugs (semivolatile vapor phase). Figure 3 shows mutagrams, plots of mutagenic activity against the HPLC fraction number with increasing HPLC fraction number corresponding to increasing polarity, of the vapor-phase and particle-phase extracts. This direct-acting ambient air mutagenicity cannot be due to the PAH themselves, because the PAH require microsomal activation for expression of their mutagenicity. The nitro-PAH are strong, direct-acting mutagens (*2*) and elute in the HPLC fraction 4 for the HPLC program used by Harger et al. (Figure 3) (*89*). For the samples collected and tested for mutagenic activity shown in Figure 3, the total direct-acting mutagenicity in the vapor-phase PUF plug sample was actually higher than that in the particle-phase filter sample (210 revertants $m^{-3}$ for the vapor-phase sample versus 160 revertants $m^{-3}$ for the particle-phase sample) (*89*), showing the potential importance of vapor-phase mutagens in the atmosphere.

While the vapor-phase sample contained approximately 50% of the overall mutagenicity in the nitro-PAH-containing fraction 4, the majority (94%) of the mutagenicity in the particle-phase sample was due to compound classes more polar than the nitro-PAH (Figure 3) (*89*). Mutagrams of particle extracts using the

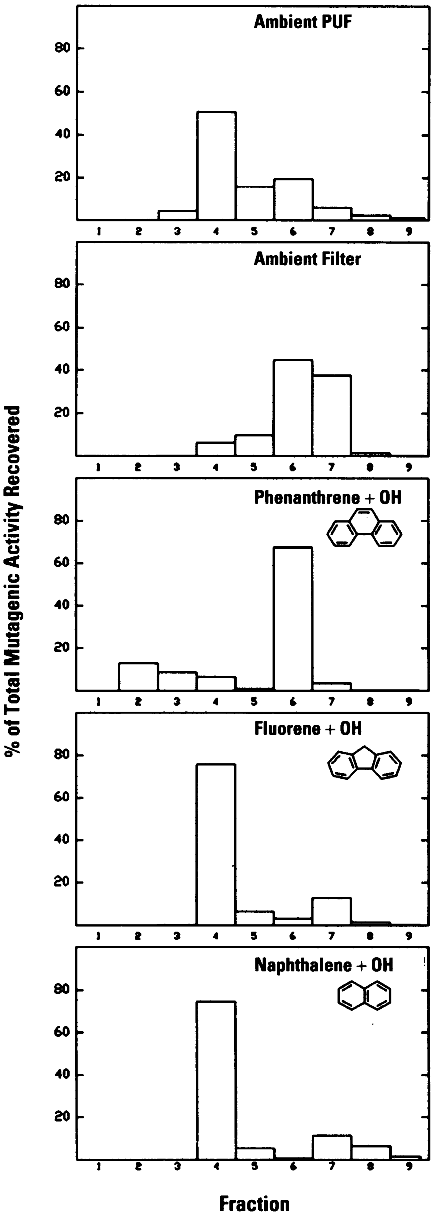


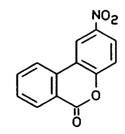

**Figure 3.** Mutagrams (using the microsuspension modification of the Ames assay) of ambient polyurethane foam solid adsorbent and filter sample extracts from Clairmont, California, and of extracts of polyurethane foam solid adsorbent samples collected from environmental chamber OH radical-initiated reactions of naphthalene, fluorene, and phenanthrene (*19,89*).

standard Ames plate incorporation assay also show profiles with more activity in the more polar fractions (*17,18,90*). From the measured concentrations of nitrofluoranthenes and nitropyrenes in several particulate samples and their mutagenic activities (in the standard assay), it was calculated that the nitrofluoranthenes and nitropyrenes contributed less than or equal to 10% of the direct-acting mutagenicity of these extracts (*26,91*). Furthermore, the direct-acting mutagenicity of a series of ambient air filter samples collected at seven sites in California did not correlate with the PAH concentrations but rather with the 2-nitropyrene concentrations (*26*). Because 2-nitropyrene is formed in the atmosphere from the OH radical-initiated reaction of gas-phase pyrene, the remainder of the ambient air direct-acting mutagenicity may be associated with the OH radical reaction products of organic compounds and may be due to the mutagenicity of the 2- to 4-ring PAH reaction products other than the nitro-PAH. For example, it is interesting that the nitro-PAH account for 5% or less of the products of the gas-phase OH radical-initiated reactions of the 2- to 4-ring PAH (Table 3) and 10% or less of the ambient air particle-phase, direct-acting mutagenicity.

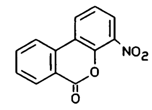
Environmental chamber studies of the gas-phase, OH radical-initiated reactions of naphthalene, fluorene, and phenanthrene have been carried out (*19,20,58,59*), with 2000- to 4000-L volume gas samples being collected from the chamber for HPLC fractionation with subsequent mutagenicity testing (using the microsuspension modification of the standard plate incorporation assay) and chemical analysis by GC-MS. The mutagrams obtained from these chamber OH radical-initiated reactions of naphthalene, fluorene, and phenanthrene are shown in Figure 3.

For the naphthalene and fluorene reactions, the mutagrams exhibit profiles in which the majority of the activity is in fraction 4, which contains nitro-PAH. Chemical analyses showed the presence in the HPLC fraction 4 of 1- and 2-nitronaphthalene from naphthalene (*19*) and 1-, 2-, 3-, and 4-nitrofluorene (with 3-nitrofluorene being the dominant isomer) from fluorene (*19,58*). Use of the mutagenic activities of the nitronaphthalenes and nitrofluorenes (*19*) showed that the nitronaphthalenes, in particular 2-nitronaphthalene, accounted for approximately 90% of the activity of fraction 4 of the naphthalene reaction products and that the nitrofluorenes, in particular 3-nitrofluorene, accounted for approximately 75% of the activity of fraction 4 of the fluorene reaction products (*19*). The nitronaphthalenes and nitrofluorenes are present in the atmosphere mainly in the gas phase (*24,28,58*), and these volatile nitro-PAH contribute to the observed vapor phase fraction 4 mutagenicity. It is expected that the nitronaphthalenes and methylnitronaphthalenes are significant contributors to the observed vapor-phase fraction 4 mutagenicity (*89*) because 2-nitronaphthalene accounted for approximately 13% of the activity of fraction 4 of the vapor phase sample shown in Figure 3 and the methylnitronaphthalenes are abundant in southern California ambient air (*11,24,92*).

In contrast to the mutagenicity profiles from the naphthalene and fluorene reactions, the majority of the mutagenic activity from the phenanthrene reaction products resides in fraction 6, an HPLC fraction more polar than the nitro-PAH and therefore is generally similar to the particle-phase ambient air mutagenicity profile. Chemical analysis showed the presence of the mutagenic 2-nitro-6H-dibenzo[*b,d*]pyran-6-one (Structure I) and 4-nitro-6H-dibenzo[*b,d*]pyran-6-one (Structure II) in this mutagenic fraction 6 of the phenanthrene reaction products.




(I)




(II)

Based on the mutagenic activities of these two nitrodibenzopyranones in the microsuspension assay (*19,89*), the 2-isomer accounted for all of the mutagenicity in fraction 6 of the phenanthrene reaction products (*20,59*). Moreover, 2- and 4-nitrodibenzopyranone were observed in both the gas and particle phases (but mainly in the particle phase) in ambient air samples collected in southern California (*20,59*). The nitrodibenzopyranones were also found in the National Institute of Standards and Technology Standard Reference Material 1649 urban dust collected in Washington, DC (*59*), as well as in ambient air samples collected in Boise, Idaho, and Philadelphia, Pennsylvania (J. Lewtas and M. G. Nishioka, personal communication).

For four particle and vapor-phase samples on which we have conducted HPLC fractionation with mutagenicity testing of the individual fractions, the 2-nitrodibenzopyranone accounts for essentially all of the mutagenic activity in fraction 6 of both the vapor-phase and particle-phase samples (*59*). Moreover, the 2-nitrodibenzopyranone accounted for approximately 20% of the total direct-acting mutagenicity in the microsuspension assay of the crude extract of a Riverside, California, ambient air particle sample (*20*).

In addition to the 2- and 4-nitrodibenzopyranones, seven nitro-PAH lactones [tentatively identified as methylnitrodibenzopyranones (molecular weight 255) and nitrophenanthropyranones (molecular weight 265)] have been tentatively identified by GC-MS in an extract from ambient particulate samples collected in Riverside, California (*20*). Thus, although the proportion of the ambient activity attributable to the nitrodibenzopyranones or to any individual compound or class of compound will be dependent upon the assay system used [(*19*); J Lewtas, MG Nishioka, personal communication], it is likely that nitro-PAH lactones formed in the atmosphere will prove to be an important class of ambient mutagens.

NOTE ADDED IN PROOF. Recent kinetic (*93*) and product (*94*) studies show that the hydroxycyclohexadienyl radicals formed from OH radical addition to benzene, toluene, and the xylenes react with both $O_2$ and $NO_2$, with the $O_2$ reaction dominating under tropospheric conditions. However, Atkinson et al. (*95*) have shown that the rate constant for reaction of the $NO_3$-naphthalene adduct, formed by addition of the $NO_3$ radical to naphthalene, with $NO_2$ is $>2.5 \times 10^6$ higher than that for reaction of the adduct with $O_2$ at 298 K. The ratio of the rate constants for the corresponding reactions of $NO_2$ and $O_2$ with the OH-naphthalene adduct may be expected to be similar to those for the $NO_3$-naphthalene adduct. The $NO_2$ reactions with the OH-naphthalene and $NO_3$-naphthalene adducts may then dominate in urban and rural air masses (*95*).

The rate constants given in Table 2 for the reactions of phenanthrene and anthracene with the OH radical are superseded by those recently measured by Kwok et al. (*96*) of $1.3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for both phenanthrene and anthracene at 296 ± 2 K. Additionally, Kwok et al. (*96*) obtained rate constants for the $NO_3$ radical and $O_3$ reactions with phenanthrene of $\{1.2 \times 10^{-13} + 7.0 \times 10^{-28} [NO_2]\}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ and $4 \times 10^{-19}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, respectively, at 296 ± 2 K.

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